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The use of a steady state flow reactor in the study of rapid gas phase reactions

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THE USE OF A STEADY STATE FLOW REACTOR IN THE STUDY OF RAPID GAS PHASE REACTIONS

BY

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A

THESIS

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INTRODUCTION

The demonstration of the feasibility of rocket propelled devices for various purposes within the past few years has initiated an intensive search for suitable reactants for use as rocket fuels. Consequently, the investigation of the properties of chemical reactions which rapidly liberate large quantities of energy has assumed major importance. In order that such reactions may be adapted to practical use as rocket propellants knowledge of the characteristics of these reactions is required. Properties such as+ the mechanism of the reaction, the speed of the reaction under varied conditions of temperature, pressure and concentrations, the conditions required for the initiation of the reaction, and the energy to mass ratio of the reaction system are of prime importance.

A reaction typical of the type used as rocket propellants, the reaction between ammonia and nitrogen dioxide, was selected for investigation at the Missouri School of Mines and Metallurgy. This particular reaction was chosen because of the ready availability of the materials commercially, their relatively low cost, the ease and safety of their storage, their high theoretical heat of reaction and their rapid rate of reaction in the gas phase.

Crocker[1] instigated the study of the reaction using a constant volume, constant temperature reactor, following the reaction by pressure measurements and determining the probable net reaction by analysis of the products of the completed reaction. Burch[2] and Dillender[3] carried on an extension of this work using similar methods. This method proved inadequate in that the actual temperatures of the reaction at the observed pressures were not known, therefore, little could be determined of either the order of reaction or of the reaction velocity constant.

Burch further explored the possibilities of following the progress of the reaction optically in a continuous flow system= the reactants being diluted with an inert gas to minimize the temperature rise during the reaction and the progress of the reaction followed by observation of the changes in transmittancy of the colored gas NO_2. It was found that the solid substances formed in the reaction, even at very low concentrations, obscured the optical measurements and this method for following the reaction proved

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(1) Crocker, H. W., M. S. Thesis, Missouri School of Mines and Metallurgy, 1951

(2) Burch, W. D., M. S. Thesis, Missouri School of Mines and Metallurgy, 1951

(3) Dillender, G., M. S. Thesis, Missouri School of Mines and Metallurgy, 1951

infeasible.

In view of the above it was decided to approach the problem in a different manner. It was felt that an essentially adiabatic, continuous flow reactor operating at a steady state would permit use of the high heat of reaction for following the progress of the reaction. By operating at steady state temperature conditions the reaction progress could be followed by observation of temperatures at specific distances in the reactor. Time intervals of contact of the reactants could be determined from the distance and rate of flow in the reactor and from this information the reaction velocity constant calculated.

This study concerns the design of a reactor and its accessories to achieve this end. Further to develop a method for determination of the reaction velocity constant for the gas phase reaction between ammonia and nitrogen dioxide at atmospheric pressure from the data obtained.

LITERATURE SURVEY

Little specific information on the reaction between ammonia and nitrogen dioxide is to be found in the literature. Besson and Rosset[4] in 1906 reported the products of the reaction as nitrogen, ammonium nitrate, nitric oxide, nitric acid and water but gave little specific information as to the conditions of the reaction. Beekhuis[5] in 1935 obtained a patent for the production of ammonium nitrate from a continuous flow, vapor phase reaction of ammonia, nitrogen dioxide and oxygen with the reaction system held to temperatures below 125°C. Patry et al[6] in 1947 reported the products of the reaction to be ammonium nitrate, ammonium nitrite, nitrogen, water and hydrazine with temperatures held to below 100°C. They further suggested that the ammonium nitrite formed reacted with excess nitrogen dioxide to form ammonium nitrate and nitric oxide, but presented no substantiating data.

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(4) Besson and Rosset, "Action du peroxyde d'azote sur l'ammoniac et quelques sais ammoniacaux", Compt. Rend., Vol. 142, pp. 633-34 (1906)

(5) Beekhuis, H. A., U. S. Patent 2,011,704 Process and Apparatus for the Vapor Phase Production of Ammonium Nitrate (1935)

(6) Patry, M., Garlet, R., and Pupko, S., "Sur les reactions entre les Oxydes d'azote et l'ammoniac", Compt. Rend., Vol. 225, pp. 941-42 (1947)

Cooley et al[7] in 1951 reported the products of reaction under constant volume conditions as ammonium nitrate, ammonium nitrite, nitrogen, water and oxygen and explored the probability of numerous possible reactions from a thermodynamic approach. Burch[8] and Dillender[9] in 1952 reported the products of reaction at constant volume and 35°C as ammonium nitrate, ammonium nitrite, nitrogen, water, oxygen and nitrous oxide. No specific information could be found in the literature concerning the products of reaction at elevated temperatures or low concentrations.

General references in the literature to kinetic study of gas phase reactions may be found in "Chemical Kinetics" by Laidler[10], "The Theory of Rate Processes" by Glasstone, Laidler and Eyring[11], "The Kinetics of Homogeneous Gas

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(7) Cooley, R. A., Russell, R. R., Crocker, H. W., Annual Report on Study of Chemical Kinetics of Rapid Reactions, Atomic Energy Commission. Unpublished. (1951)

(8) Burch, op. cit., p.2

(9) Dillender, op. cit., p.2

(10) Laidler, K. J., Chemical Kinetics, McGraw Hill, N. Y. (1950)

(11) Glasstone, S., Laidler, K. J., Eyring, H., The Theory of Rate Processes, McGraw Hill, N. Y. (1941)

Reactions" by Kassel[12] and "Experimental Methods in Gas Reactions" by Farkas and Mehlville[13].

Other than work done at the Missouri School of Mines and Metallurgy, no reference could be found in the literature concerning the kinetics of the ammonia, nitrogen dioxide reaction.

Studies have been made of the kinetic of the reaction of nitrogen dioxide with formaldehyde Pollard and Wyatt[14], carbon monoxide Brown and Crist[15], ozone Johnson[16] and sulfur dioxide Illarinov[17] all under constant volume conditions.

Methods of evaluating reaction velocity constants in continuous flow systems and the validity of following the

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(12) Kassel, L. S., The Kinetics of Homogeneous Gas Reactions, Chemical Catalog Co, N. Y., (1932)

(13) Farkas, A., and Mehlville, H. W., Experimental Methods in Gas Reactions, MacMillan, N. Y., (1939)

(14) Pollard, F. H., Wyatt, R. M. H., Fara Sec p. 760 (1949)

(15) Brown, F. B., Crist, R. H., J. Chem. Phy. Vol. 9, p 840 (1941)

(16) Johnson, H. S., Yost, D. M., J. Chem. Phy. Vol. 17, p 386 (1949)

(17) Illarinov, J. Phyic Chem. Soc Russ Vol. 14, p 1428, (1940)

progress of a reaction by the disappearance of a reactant or appearance of a product are reported by Reiser and Watson[18] and Myers and Watson[19].

The theory of homogeneous continuous flow gas phase reactions and methods of evaluating order of reaction and reaction velocity constants are given by Hougen and Watson [20].

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(18) Reiser, C. O., Watson, K. M., Natl. Pet. News, Vol. 38, p. R260 (April 1946)

(19) Myers, P. S., Watson, K. M., Natl. Pet. News, Vol. 38, p. R388 (May 1946)

(20) Hougen, O. A., Watson, K. M., Chemical Process Principles, Part III, John Wiley and Sons, Inc., N. Y. (1949)

REACTOR DESIGN

The original plan of this study was to construct a six foot reactor of one inch "teflon" rod bored 1/4" through the longitudinal axis, and locating thermocouple wells at 6" intervals and a 2" teflon mixing chamber. Because of the cost of teflon it was decided to construct a pilot model of the reactor from standard 1/8" black pipe in order to incorporate design features and improvements in the final teflon reactor.

The first preliminary reactor consisted of a 6' length of 1/8" standard black pipe with iron-constantan thermocouple junctions at 6" intervals, a standard 1/8" tee served as the mixing chamber. The flow of air and reactants were metered by flowrators. The ammonia was fed into the main stream of diluent and the nitrogen dioxide fed into the tee serving as a mixing chamber. This arrangement proved unsatisfactory in that a high concentration of nitrogen dioxide entered the main stream with low velocity and the reaction proceeded rapidly at the inlet, clogging the reactor in a very short time.

The first modification of the apparatus was to divide the diluent (air) into two streams prior to introducing the reactants. The reactants were metered into separate streams and brought together in the tee serving as a mixing chamber. Reaction again took place at the entrance to the mixing chamber and the mixing chamber soon became

clogged.

The second modification saw the replacement of the flowrator for metering air with a pair of critical flow orifices so that each air flow line would be under positive pressure. The tee serving as a mixing chamber was replaced with a chamber machined from 1 1/2" cold rolled steel rod, so constructed as to introduce the two streams of reactants at a 15° angle. This arrangement solved the problem of clogging at the mixing chamber. The two streams then seemed to mix properly and a reaction took place, as evidenced by rising temperatures down the reactor length. However, before the steady state was reached the reactor itself clogged with solid products and the build up of back pressure terminated the run.

Several attempts were made to achieve the steady state with this reactor but all ended in stoppage, the time required varying from one to fifteen minutes. The solid material causing the stoppage was analysed and found to consist chiefly of ammonium nitrate.

As increasing the diameter of the reactor was impracticable due to velocities and concentrations required, it was decided to eliminate the formation of the solid product ammonium nitrate by carrying on the reaction above 210°C, the decomposition temperature of this compound.

The problem then encountered was that of heating a small known flow of gas to the required temperature. Con-

ventional methods of passing the air stream through heated coils and heated packed tubes proved entirely inadequate. Unsatisfactory results were obtained by passing the gas through molten sodium hydroxide, the temperatures attained were adequate but the air stream was badly contaminated with fine particles of the salt. Similar attempts with molten metals gave unsatisfactory results because of the rapid oxidation of the metals.

During these trials it was noted that a stream of air impinging on a heated object rapidly cooled the object. On further investigation it was found that if a small stream of air was impinged on a heated copper plate that the air stream leaving the plate was quite hot and at about the temperature required for this purpose. Consequently, an enclosed heater applying this principle of jetting the air stream at right angles to the heating surface was constructed with successful results, achieving temperatures of 250°C at the required flow rates and considerably higher temperatures at higher flow rates. The final design of this type heater used is shown in Figure 4, page 17.

With the air preheaters installed and the reactor operating with diluent temperature of about 350°F and 10 mol % reactants, it was soon apparent that the formation of ammonium nitrate was eliminated and that the reaction which was taking place was much slower. It was noted that the introduction of the reactants, with their high specific heats, resulted in cooling of the reactant streams, in some cases

to temperatures low enough to start the formation of ammonium nitrate with consequent clogging.

In order to follow the slower reaction it was decided to increase the length of the reactor. In order to minimize the cooling effect of the reactants and to overcome heat losses in the section before mixing it was decided to introduce a tempering section in the reactant flow lines.

The final design used in the experimental work then consisted of a 14' reactor of 1/8" standard black pipe with thermocouple junctions at 10" intervals, well insulated with 1" magnesia. The tempering sections consisted of two 6' lengths of black pipe wrapped with 22 gauge monel wire with a 750 watt rating at 110 V. These heaters were controlled by variac and operated at 700°F surface temperature.

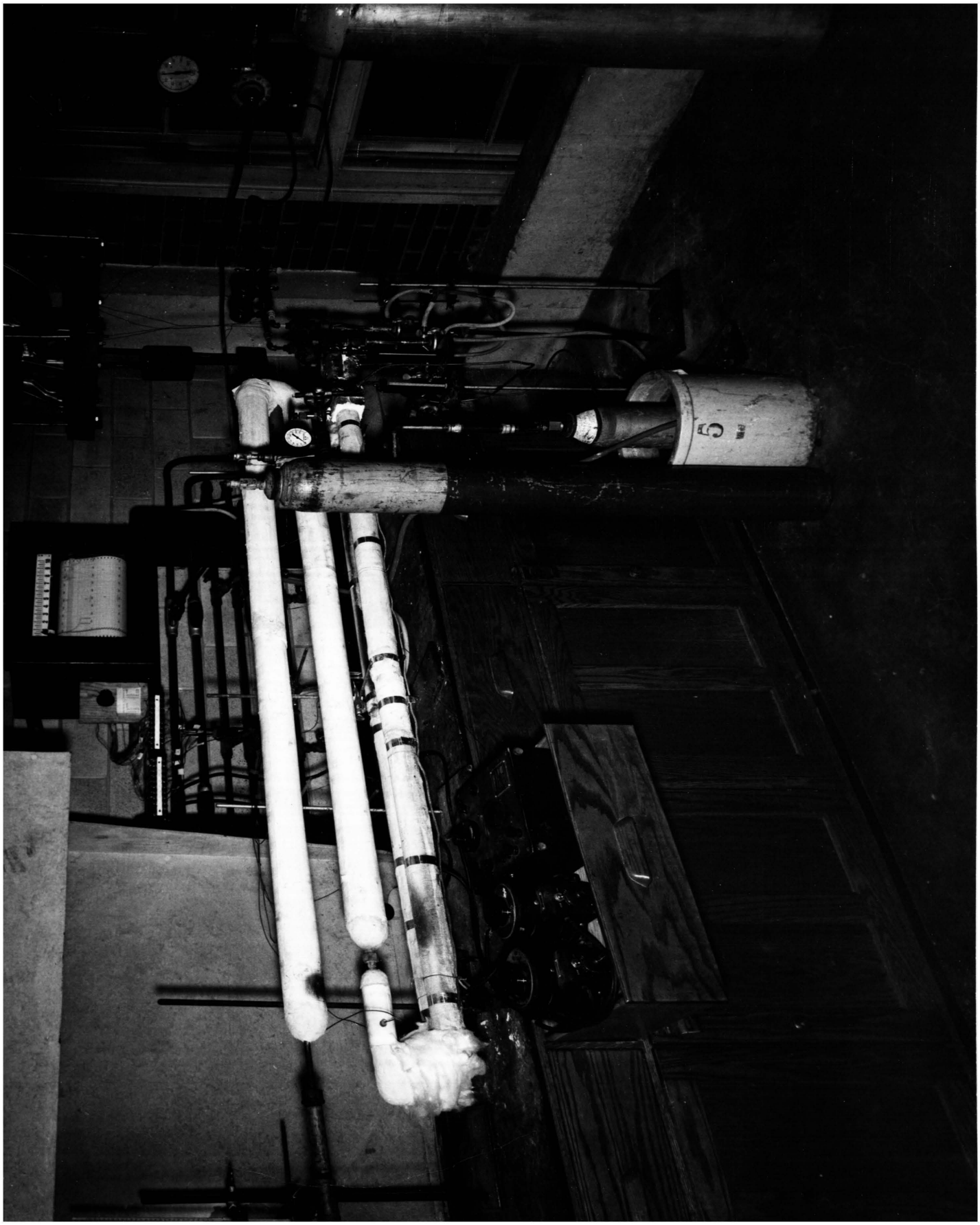
APPARATUS

A general view of the apparatus used for the experimental work in this study is shown in Figure 1, page 13. Figure 2, page 14 is a schematic diagram of the apparatus showing the essential component of the reactor and their relationship to the flow pattern of the reactor system. Figure 3, page 15 is a detail picture of the reactant metering system and the diluent pre-heaters.

In general the apparatus consists of: 1. A reactant supply system by means of which the flow of the reactants, ammonia and nitrogen dioxide and the diluent air, may be controlled to known desired amounts within the capacity of the metering devices. 2. Electrically heated tempering sections for each reactant stream to assure complete mixing of the reactant and diluent and to minimize heat losses during the mixing period. 3. A teflon mixing chamber. 4. A 14' reactor pipe with provisions for obtaining pipe temperatures at 10" intervals from the point of mixing the reactants. 5. An eight point chart temperature recorder to continuously record reactor temperatures.

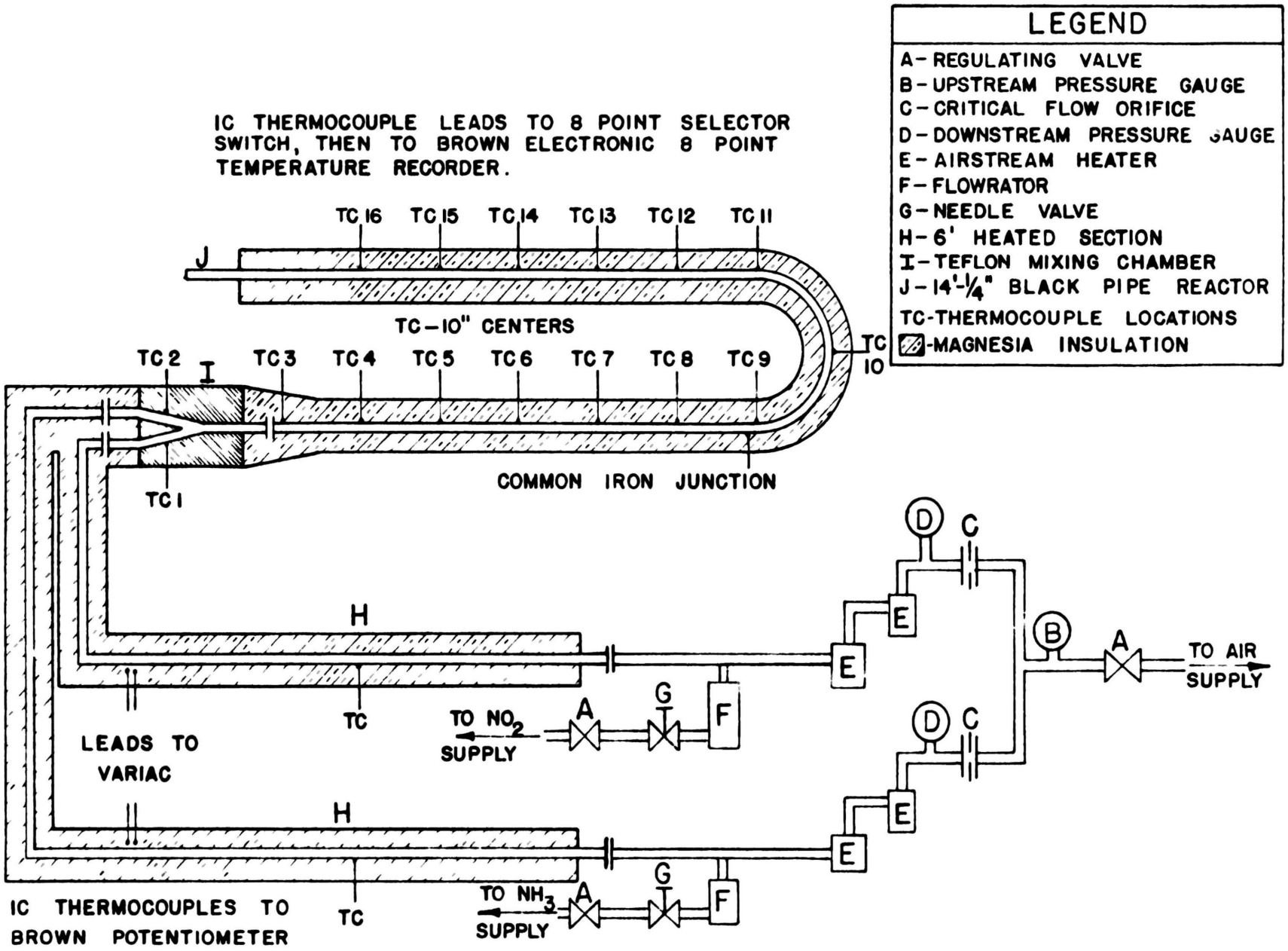
The essential components of the apparatus are:

1. Air regulating system consisting of an Airco Regulating Valve, equipt with a 0 - 150 psi gauge, a set of two critical flow orifices made of 12 gauge 14S aluminum sheet punched disks 3/4" diameter, center drilled 0.023", counter drilled for half thickness to 0.050" and inserted



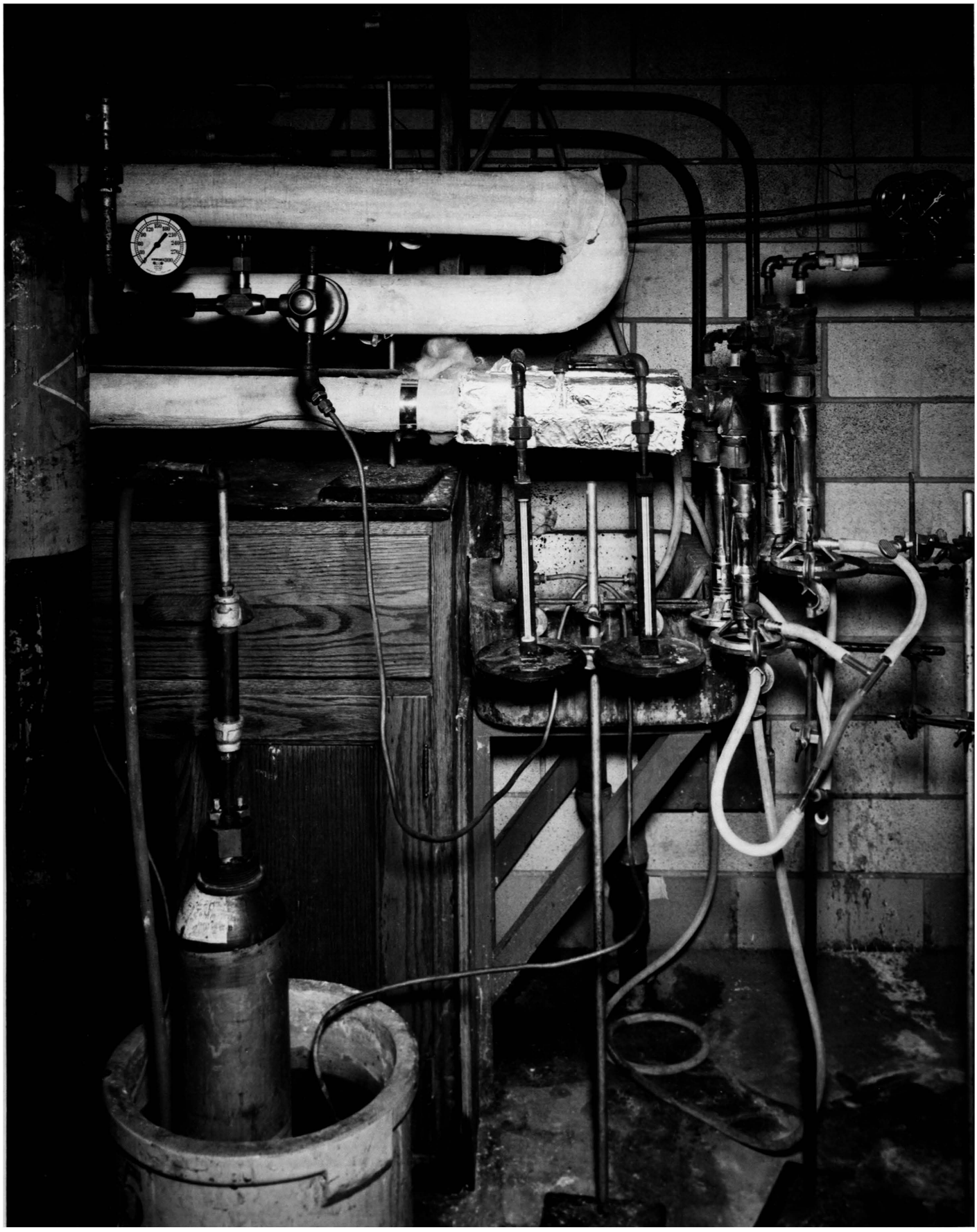
GENERAL VIEW OF THE APPARATUS

Figure 1



SCHEMATIC DIAGRAM OF APPARATUS

Figure 2



DETAIL VIEW OF REACTANT METERING SYSTEM

Figure 3

in the air supply lines in specially adapted 1/4" ground joint standard pipe unions.

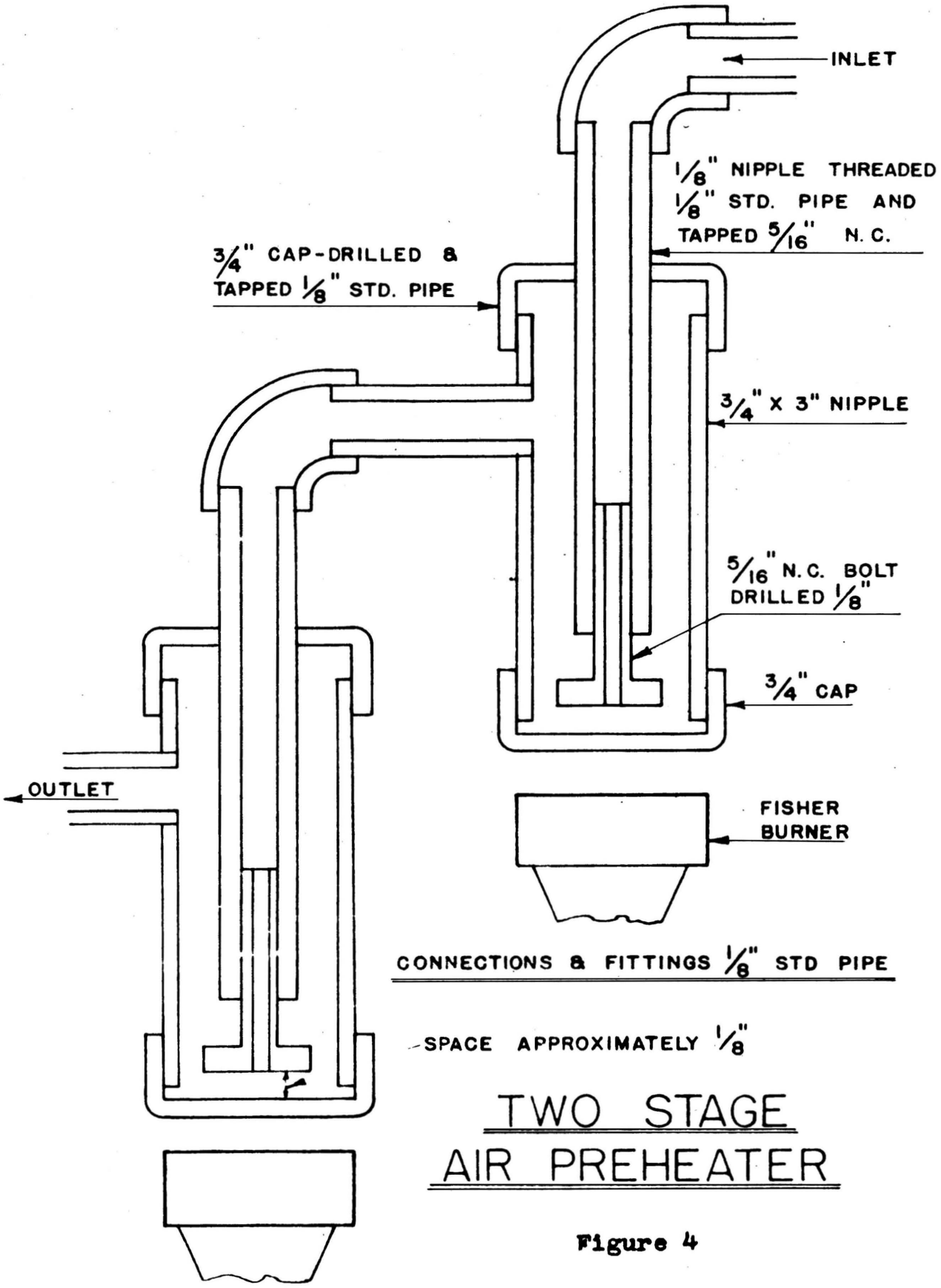
2. Air pre-heaters consisting of an original design two stage gas heater, details of construction are shown in Figure 4, page 17.

3. NO_2 flow system consisting of a NO_2 cylinder heated to 60°C in a thermostaticly controlled water bath, a tempering coil also immersed in the water bath, a standard 1/8" needle valve and a Fisher-Porter Flowrator using tube No. 06-150/13 with 3/16" stainless steel float.

4. NH_3 flow system consisting of NH_3 cylinder, regulating valve, standard 1/8" needle valve and a Fisher-Porter Flowrator using tube No. 06-150/13 with 3/16" stainless steel float.

5. Two tempering heaters one for each the NO_2 and NH_3 streams consisting of 6' sections of 1/8" standard steel pipe wrapped with No. 22 gauge monel wire having a rating of 750 watts each at 110V. Each heater was insulated with 1" of magnesia, provided with a thermocouple at the mid-point and a 1000 watt variac control.

6. Mixing chamber of 2" moulded teflon rod provided with inlets for each of the reactant streams and a common outlet. The chamber is so constructed as to introduce the reactants into a common stream at a 15° angle. Each stream was provided with a thermocouple well just before the point of mixing to measure the temperature of the reactant gas



TWO STAGE AIR PREHEATER

Figure 4

streams entering the reactor.

7. Reactor: A fourteen foot 1/8" standard iron pipe with a 180° bend of 2 1/2" radius at the mid point. The reactor was fitted with thermocouple junctions at 14 - 10" intervals from the point of mixing of reactants in the mixing chambers. Thermocouple junctions were made by crimping constantan wire in surface of the pipe, the pipe itself being used as the iron portion of the couple. The entire reactor section was insulated with 1" magnesia.

8. Selector Switch: A standard 8 point single pole double throw wafer switch to permit recording of 16 points with an 8 point recorder by two position switching.

9. Minneapolis-Honeywell 8 point recorder Model 153X60P8-X-31 calibrated for iron constantan thermocouples, range 0-1000°F.

10. 16 iron constantan thermocouple junctions, two measuring the temperatures of the mixed reactant - diluent streams just prior to mixing and 14 measuring pipe wall temperatures at 10" intervals from the point of mixing of reactants.

EXPERIMENTAL PROCEDURE

The following procedure was used in making the experimental runs for this study:

1. The NO_2 water bath was brought to approximately 60°C with live steam, the controlled electric heaters turned on and bath temperature stabilized at 60°F.

2. The diluent stream was turned on and the pressure adjusted to 60 psig to speed the initial heating of the reactor system. The initial heating was continued until the temperature at various reactor points had reached an approximate steady state.

3. The burners under the air pre-heaters were lit and adjusted so that the temperatures of the diluent streams entering the mixing chamber were approximately equal.

4. The Brown recorder chart started. The electronic balancing mechanism of this instrument was not turned off during the series of runs to assure stability as recommended by the manufacturer.

5. The heaters of the tempering sections were turned on and adjusted to operate at 700°F surface temperature as indicated by 1-C thermocouples located at the mid-point of each section attached to a Brown Potentiometer. To this point the heat loss runs and reactant runs were identical. After the entire reactor system had reached the operating conditions outlined above the experimental runs were begun.

Heat Loss Runs No. 1, No. 4 and No. 11

The pressure of the diluent stream was adjusted to 50 psig, the selector switch positioned to record points 9-16 on the temperature recorder and the reactor operated until the indicated temperatures of points 9-16 were stabilized. The selector switch was then used to record the temperatures of points 1-16 in sequence and the reactor operated until these points showed no change of temperature for a 20 minute period. This condition was taken as a steady state. Having reached a steady state temperature readings were taken and recorded for each of points 1-16. The data so obtained was used in the calculation of heat losses from the reactor at ambient conditions of approximately 80°F.

Reaction Runs No. 3, No. 6, No. 7 and No. 8

The pressure of the diluent stream was adjusted to the pressure desired for the run. The ammonia stream was then turned on and the flow adjusted with a needle valve to a flowrator reading of 12.5. The nitrogen dioxide stream was then turned on and adjusted with a needle valve to a flowrator reading of 12.5. The selector switch was adjusted to record the temperatures of points 9-16. The reactor was then operated at these flow conditions until the temperatures of points 9-16 were stabilized. The selector switch was then used to record the temperatures of points 1-16 in sequence and the reactor operated until the temperatures at all points of the reactor remained constant for a period of 20 minutes, which condition

was taken as a steady state. Having reached a steady state temperature readings for each point of the reactor were taken and recorded. The data so obtained was used in the calculation of the reaction velocity constant for the reaction.

CALIBRATIONS

Calibrations of the metering devices were made prior to the experimental runs. The methods of calibration were as follows:

Critical Flow Orifices: Calibration was made by determining the time required to displace 300 pounds of water at 68°F from a 55 gallon drum placed on a platform balance. Runs were made at 5 psi intervals from 15 to 60 psig. Corrections were made for final pressure of air in the drum and humidity, assuming saturation. Results were calculated in pounds of dry air per minute and are summarized in Table XI.

Fischer-Porter Flowrators Tube No. 06-150/13 3/16" stainless steel float:

Calibration nitrogen dioxide: The nitrogen dioxide after passing through the flowrator was absorbed in a known volume of standard potassium permanganate acidified with sulfuric acid contained in a flask equipt with a water seal and magnetic stirrer. The flow of nitrogen dioxide was adjusted by needle valve to the desired reading of flowrator while the gas stream was allowed to escape through the outlet of three-way stop cock, flow was then diverted to the absorbing flask and timing started. Flow was continued until the potassium permanganate solution was just decolorized, at which time flow was stopped and the total time of flow observed. The absorbing medium was

then back titrated with standard potassium permanganate and the total flow of nitrogen dioxide for the measured time interval calculated in gram moles per minute. Duplicate runs were made at flowrator readings of 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0, 13.0, and 14.0 and average values used. Results of this calibration are summarized in Table XII.

Calibration ammonia: The ammonia after passing through the flowrator was absorbed in a known volume of standard hydrochloric acid with methyl-orange present as an indicator. The apparatus and method used was identical with that used for the calibration with nitrogen dioxide. The rate of flow was calculated in gram moles per minute. Duplicate runs were made with flowrator readings 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0, 13.0 and 14.0 and average values used. The results of this calibration are summarized in Table XII.

DATA

Data are presented here for seven experimental runs of two types. The data consists of temperatures observed at 10" intervals of reactor length with the reactor operating at the steady state and the amounts of reactants and diluent used for the run.

Blank Runs: Three blank runs (Runs No. 1, 4 and 11) were made to establish the heat losses from the reactor at ambient temperature of 80°F. In each of these runs the reactor flow consisted of 2.996 pounds of air per hour with no reactants being used. The data for these runs are summarized in Table I page 25.

Reactant Runs: Four reactant runs were made (Runs No. 3, 6, 7, and 8) to be used to follow the progress of the reaction after applying the necessary corrections for heat losses for the reactor as established in the blank runs. For these runs the flow of reactants was held constant at 0.0105 pound moles nitrogen dioxide per hour and 0.0158 pound moles ammonia per hour. Diluent flow was varied using 1.501 pounds of air per hour in Runs No. 6 and 8, 1.748 pounds of air per hour in Run No. 3 and 1.262 pounds of air per hour in Run No. 7. The data for these runs are summarized in Table II page 26.

TABLE I

DATA SUMMARY

HEAT LOSS RUNS

REACTOR LENGTH	REACTOR TEMPERATURES °F		
INCHES	RUN NO. 1	RUN NO. 4	RUN NO. 11
00	418	428	
10	308	312	528
20	272	279	435
30	242	253	358
40	225	234	307
50	210	217	273
60	197	203	244
70	189	190	
80	175	173	
90	162	162	
100	155	153	
110	148	144	
120	144	137	
130	137	130	
140	133	125	
AIR PRESSURE psig	50	50	50
AIR FLOW lb/hr	2.996	2.996	2.996

TABLE II

DATA SUMMARY

REACTION RUNS

REACTOR LENGTH INCHES	REACTOR TEMPERATURES °F RUN NO. 3	RUN NO. 6	RUN NO. 7	RUN NO. 8
00	417	417	400	477
10	341	334	332	368
20	323	324	312	344
30	319	297	305	324
40	282	282	292	311
50	267	270	283	305
60	254	261	274	296
70	242	252	267	287
80	234	244	259	277
90	231	237	254	271
100	230	233	252	268
110	247	226	244	263
120	206	223	243	255
130	195	221	241	265
140	184	217	236	261
AIR PRESSURE psig	25	20	15	20
AIR FLOW lb/hr	1.748	1.501	1.262	1.501
NO_2 FLOW Moles/hr X 10^4	105	105	105	105
NH_3 FLOW Moles/hr X 10^4	158	158	158	158

CALCULATIONS

Calculation of Heat Losses From the Reactor:

In order to calculate the heat losses of the reactor from the data obtained from Run No. 1, Run No. 4, and Run No. 11 a method of successive approximations was used. Summary of these calculations are given in Tables III page 28, IV page 29 and Table V page 30. The method may be described as follows:

1. The heat losses for each 10" section were calculated for each run assuming gas temperatures equal to pipe temperatures.

2. The heat loss in Btu/hr 10" was plotted as a function of mean pipe temperature.

3. Making use of the plot from step 2 the gas temperature corresponding to the observed pipe temperature at the 10" point was calculated for Runs No. 1 and 4 and the coefficient of heat transfer, h, between the gas stream and pipe wall calculated.

4. Making use of an average h for the two runs and assuming h to be constant throughout the length of the reactor the value of the gas temperature corresponding to pipe temperatures at 25°F intervals over the range of temperatures encountered in the experimental runs, were calculated. The calculated gas temperatures were plotted as a function of pipe temperature.

5. Using the plot from step 4, a second trial was made using calculated gas temperatures corresponding to

TABLE III

HEAT LOSS CALCULATIONS

RUN NO: 1 TRIAL NO. 3

2.996 lb air/hour

REACTOR LENGTH INCHES	PIPE TEMP °F	MEAN PIPE TEMP °F	GAS TEMP °F	MEAN GAS TEMP °F	Δ TEMP °F	mC_p $\frac{Btu}{lb\ °F}$	Q $\frac{Btu}{Hr\ IO^n}$
00	418		418				
10	308	345	351	385	67	0.7323	49.1
20	272	287	304	328	47	0.7275	34.2
30	242	255	267	286	37	0.7258	26.9
40	225	237	243	255	24	0.7242	17.4
50	210	218	226	235	17	0.7230	12.3
60	197	204	210	218	16	0.7220	11.6
70	189	193	201	206	9	0.7217	6.49
80	175	182	185	193	16	0.7207	11.5
90	162	168	168	172	17	0.7202	12.2
100	155	158	162	165	6	0.7200	4.32
110	148	151	155	159	7	0.7197	5.04
120	144	146	151	153	4	0.7195	2.88
130	137	140	143	147	8	0.7191	5.75
140	133	135	140	142	3	0.7189	2.16

TABLE IV

HEAT LOSS CALCULATIONS

RUN NO. 4 TRIAL NO. 3

REACTOR LENGTH INCHES	PIPE TEMP °F	MEAN PIPE TEMP °F	GAS TEMP °F	MEAN GAS TEMP °F	Δ TEMP °F	mC_p $\frac{Btu}{lb\ °F}$	Q $\frac{Btu}{Hr\ IO^n}$
00	428		428				
10	312	355	355	392	73	0.7327	53.5
20	279	295	312	334	43	0.7285	31.3
30	253	265	280	296	32	0.7265	23.2
40	234	240	256	268	24	0.7250	17.4
50	217	222	234	245	22	0.7237	15.9
60	203	210	217	226	17	0.7227	12.3
70	190	196	201	209	16	0.7220	11.6
80	173	182	183	192	18	0.7206	13.0
90	162	168	168	175	15	0.7203	10.8
100	153	158	160	164	8	0.7199	5.76
110	144	148	151	155	9	0.7197	6.47
120	137	140	143	147	8	0.7193	5.75
130	130	134	136	140	7	0.7189	5.03
140	125	128	130	133	6	0.7187	4.31

TABLE V
HEAT LOSS CALCULATIONS

RUN NO: 11 TRIAL NO. 3

REACTOR LENGTH INCHES	PIPE TEMP °F	MEAN PIPE TEMP °F	GAS TEMP °F	MEAN GAS TEMP °F	Δ TEMP °F	mC_p $\frac{Btu}{lb\ °F}$	Q $\frac{Btu}{Hr\ IO"}$
10	528						
20	435	475	550				
30	358	393	424	487	136	0.7400	99.0
40	307	335	350	387	74	0.7325	54.2
50	273	289	305	328	45	0.7275	33.2
60	244	258	269	286	36	0.7258	25.8

observed pipe temperatures to compute the heat losses from each 10" section of the reactor. These calculated heat losses were plotted as a function of mean pipe temperature for the section.

6. Making use of the plot from step 5, steps 3, 4 and 5 were repeated giving another relationship between gas temperatures and pipe temperatures which were similarly plotted.

7. As this type of successive approximation is oscillatory, values of gas temperatures intermediate to those determined in trials 1 and 2 were assumed for trial 3 and similarly plotted. Using this plot steps 3 and 4 were repeated and the gas temperatures corresponding to pipe temperatures recalculated. The values of the assumed temperatures and those calculated in trial 3 are summarized in Table VI page 32. As the assumed and calculated gas temperatures were in close agreement these values were taken as the best approximation of the relationship and were used in all further calculations. A plot of gas temperatures as a function of pipe temperature is shown in Figure 5 page 33.

TABLE VI

COMPARISON OF ASSUMED AND CALCULATED

GAS TEMPERATURES

TRIAL NO. 3

PIPE TEMPERATURE °F	ASSUMED GAS TEMPERATURE °F	CALCULATED GAS TEMPERATURE °F	DEVIATION °F
125	130	130	0
150	157	157	0
175	185	184	-1
200	213	213	0
225	243	243	0
250	275	274	-1
275	308	306	-2
300	342	339	-3
325	372	372	0
350	414	411	-3
375	451	450	-1
400	487	487	0
425	532	529	-3
450	572	572	0
		TOTAL DEVIATION	-14
		AVERAGE DEVIATION	- 1

AVERAGE h = 15.4 Btu/hr ft^2 °F

PLOTTED Figure 6

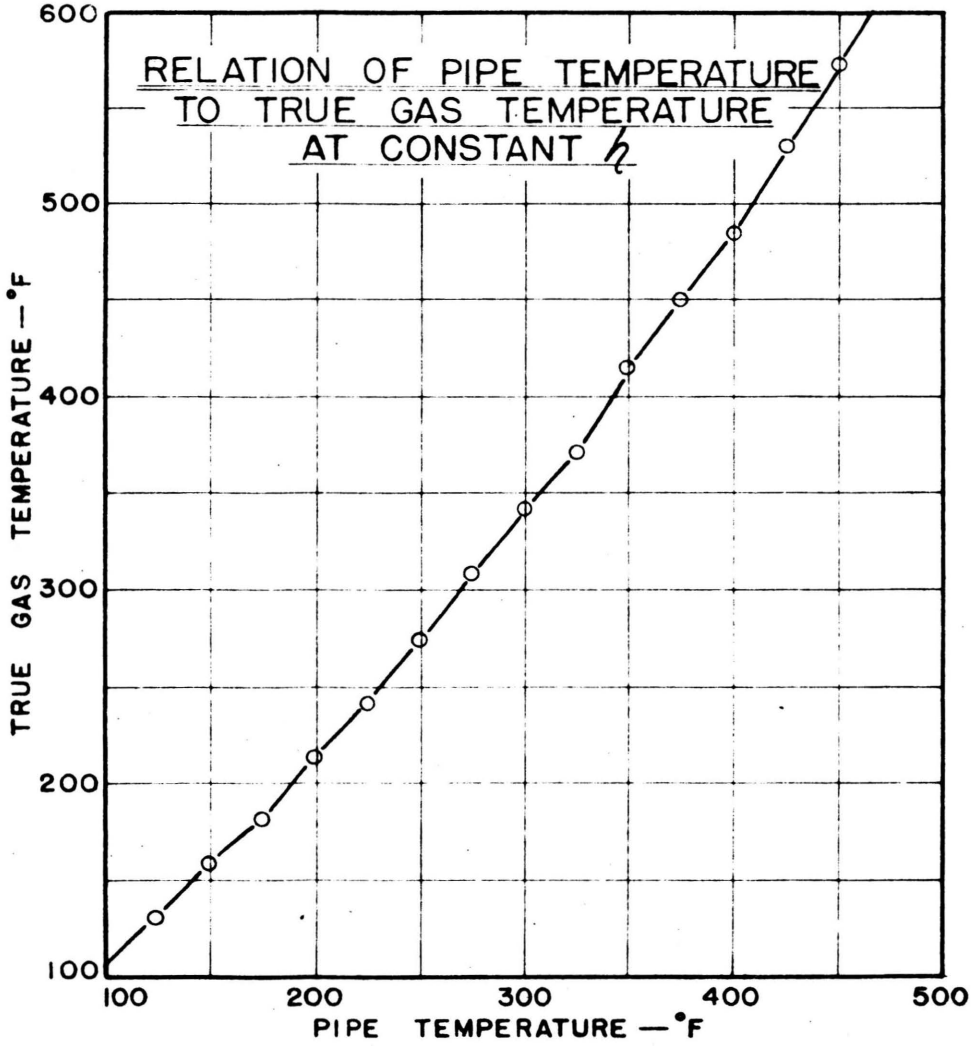

RELATION OF PIPE TEMPERATURE
TO TRUE GAS TEMPERATURE
AT CONSTANT h
TRUE GAS TEMPERATURE — °F
PIPE TEMPERATURE — °F
600
500
400
300
200
100
100
200
300
400
500

Figure 5

SAMPLE CALCULATIONS:

1. Heat Loss in Reactor Sections:

Trial 3, Run No. 1, Section 00"-10"

Tg = Temperature of the gas °F

Tga= Mean temperature of gas in section °F

Tp = Observed temperature of pipe °F

Tpa= Temperature of pipe at mid-point of section as determined from a plot of Tp versus reactor length L. °F

Q = Heat loss in the section, Btu/hr

From the data $Tg_0 = 418°F$

From Figure 5, where $Tp_{10} = 308°F$, $Tg_{10} = 345°F$

$Tga_{0-10} = (418+345)/2 = 385°F$

$$\Delta T_{0-10} = Tg_0 - Tg_{10} = 418-351 = 67°F$$

$$Q = m\ Cp\ \Delta T_{0-10}\ ,\ Cp \text{ at } Tga$$

$$Q = 2.996(0.2444)(67) = 49.1 \text{ Btu/hr}$$

Q is calculated in a like manner for each section of each run and the results plotted as a function of Tpa, Figure 6

A summary of these calculations for Runs No. 1, 4 and 11 are shown in Tables III, IV and V respectively.

2. Estimation of the Coefficient of Heat Transfer between the Gas Stream and the Pipe Wall:

From Figure 6, where Tpa = 345°F, Q = 52.0 Btu/hr

$$\Delta T = Tg_0 - Tg_{10} = Q/\ m\ Cp,\ Cp \text{ at } Tga$$

$$418 - Tg_{10} = 52.0/2.996(0.2444)$$

$$Tg_{10} = 346.7°F$$

From Figure 6, where Tp_{10} = 308°F, Q = 38.0 Btu/hr

$$Q = hA\Delta T = hA(Tg_{10}-Tp_{10})$$

$$38 = h(0.0586)(346.7-308)$$

$$h = 16.75 \text{ Btu/hr ft}^2\text{c°F}$$

A similar calculation for Run No. 4 gives:

$$h = 13.97 \text{ Btu/hr ft}^2 \text{ °F}$$

The average value for the two runs being:

$$h = 15.36 \text{ Btu/hr ft}^2 \text{ °F}$$

3. Calulation of Gas Temperatures Corresponding to Pipe Temperatures at Constant h:

$$\Delta T = Tg-Tp = Q/hA$$

$$Tg-125 = 4.5/15.36(0.0586)$$

$$Tg = 130°F$$

From Figure 6, where Tpa = 125°F, Q = 4.5 Btu/hr

Similar calculations are made at 25°F intervals to 450°F and the resulting Tg plotted as a function of Tp. A Summary of the results of this calculation are shown in Table VI.

Calculation of Reaction Velocity Constants:

In these calculations it was assumed that the primary reaction envolved is represented by the equation:

$2NO_2 + 2NH_3 = 0.5\ O_2 + 2N_2 + 3H_2O - 276{,}300$ Btu (21)

from which the following relationships were derived in terms of pound moles nitrogen dioxide consumed in the reaction:

(1) $NrNO_2 = NiNO_2 - NcNO_2$

(2) $NrNH_3 = NiNH_3 - NcNO_2$

(3) $1.5\ NcNO_2 = NrH_2O$

the products O_2 and N_2 are formed in the ratio found in air so:

(4) $NrAir = NiAir + 1.25\ NcNO_2$

(5) $Nt = Nt_i + 0.75\ NcNO_2$

where: Nc = pound moles consumed per hour

Ni = initial feed in pound moles per hour

Nt_i = total moles of gas reactor feed in pound moles per hour

Nt = total moles of gas in reactor in pound moles per hour

The heat of reaction was calculated from heat of formation data given in Lange's Chemical Handbook (22) and found to be 138,300 Btu/lb mole NO_2.

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(21) Burch, op. cit., p.2

(22) Lange, Handbook of Physical Chemistry. 6th ed. Ohio, Handbook Publishers, Inc., 1946

The heat losses from the blank runs as a function of average pipe temperature, calculated in the previous section were plotted and are shown in Figure 6 page 38. These values were used for estimating normal heat losses from the apparatus during reactant runs.

For purposes of this calculation the reaction was assumed to be of the Second Order where.

$$\frac{\delta Ca}{\delta \Theta} = K\ CaCb \quad (23)$$

then when using step wise calculations from point to point:

$$K = \frac{\frac{\Delta Ca}{\Delta \Theta}}{CaCb}$$

where, C = concentration of reactants in pound moles per cubic foot

Θ = time in seconds

A summary of the calculations the reaction velocity constants for Runs No. 3, 6, 7, and 8 are given in Tables VII, VIII, IX, and X respectively, pages 38 - 41.

An explanation of the meanings of the columns of the summaries and the method of calculation follows:

Column 1. Thermocouple identification

2. L - Length of reactor from point of mixing reactants to point of observed pipe temperatures.
3. Tp - Observed pipe temperatures at reactor length L
4. Tpa - Mean temperature of the pipe taken for the mid point of section, from a plot of Tp versus L

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(23) Hougen, Watson, op. cit. p. 7

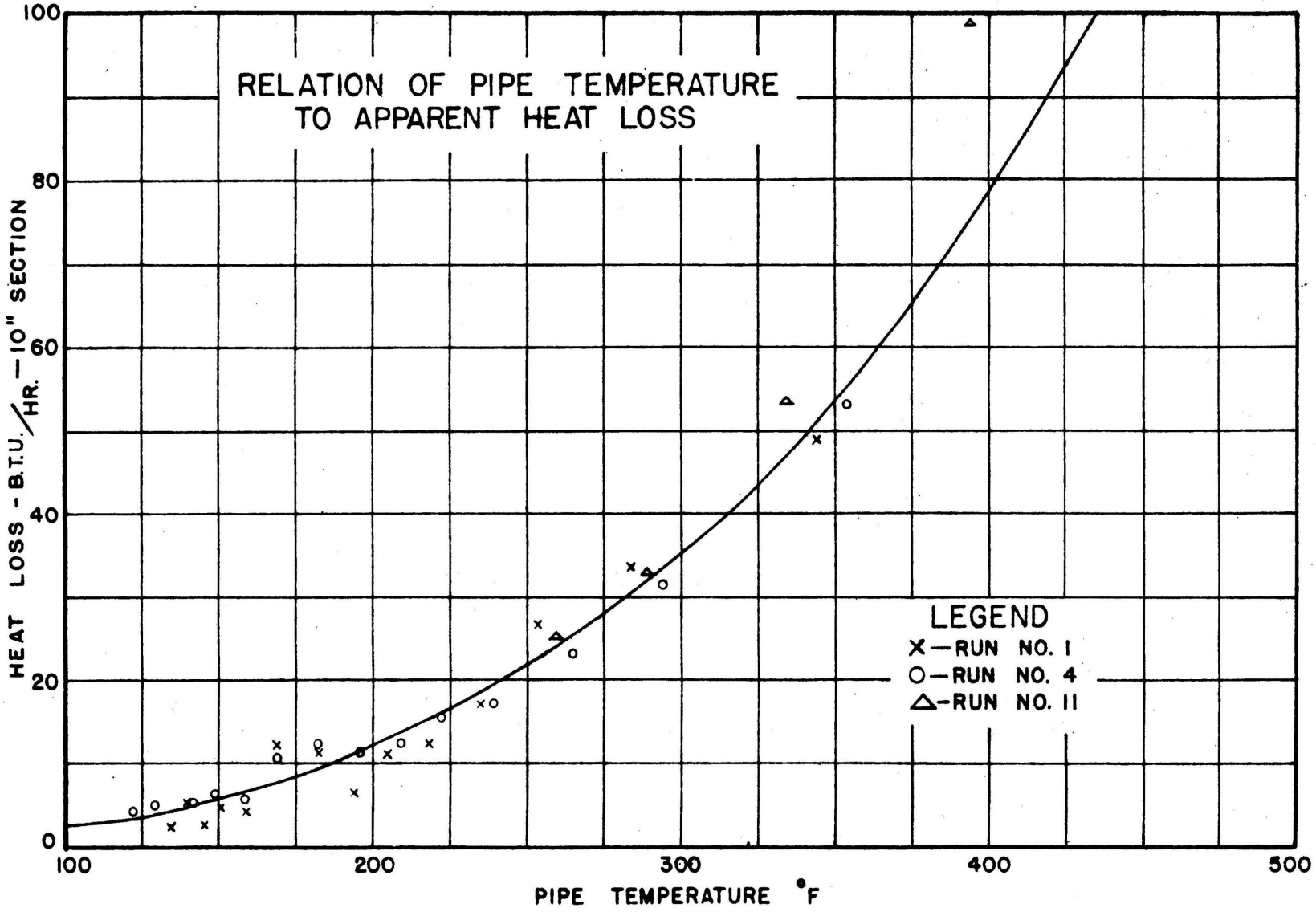
RELATION OF PIPE TEMPERATURE
TO APPARENT HEAT LOSS
HEAT LOSS - B.T.U./HR. - 10" SECTION
PIPE TEMPERATURE °F
0
20
40
60
80
100
100
200
300
400
500
LEGEND
X—RUN NO. 1
O—RUN NO. 4
△—RUN NO. 11

Figure 6

SUMMARY CALCULATIONS REACTION VELOCITY CONSTANT RUN NO. 3

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	1
POINT	LENGTH INCHES	T_p °F	T_{na} °F	T_g °F	T_{ga} °F	ΔT °F	mC_p Btu/°F HR	Q_r Btu/HR 10^4	Q_{ra} Btu/HR 10^4	Q_b Btu/HR 10^4	Q_{ba} Btu/HR 10^4	Q Btu/HR 10^2	$N_c\ NO_2 \times 10^4$ MOLES/HR	$N_r\ NO_2 \times 10^4$ MOLES/HR	$N_r\ NH_3 \times 10^4$ MOLES/HR	V FT^3/HR	$C\ NO_2 \times 10^4$ MOLES/FT^3	$C\ NH_3 \times 10^4$ MOLES/FT^3	$N_t \times 10^4$ MOLES/HR	$C\ NO_2 \times C\ NH_3 \times 10^8$ $MOLES^2/FT^6$	$\Delta\theta \times 10^2$ SEC	$\Delta N\ NO_2 \times 10^4$ MOLES/HR	$\Delta C\ NO_2 \times 10^6$ MOLES/FT^3	$\frac{\Delta C\ NO_2}{\Delta\theta} \times 10^4$ MOLES/FT^3 SEC	$K \times 10^3$ $\frac{FT^3}{MOLES\ SEC}$	T_{ga} °R	POINT
1	00	419	417																								1
2	00	414		417										105.00	158.00	54.81	1.916	2.883	866.00								2
3	10	341	364	396	407	21	0.690	14.5	14.5	60.5	60 5	46 0	3 33	101.67	154 67	53.43	1.903	2.895	868.50	5.509	2.219	3.33	6.230	2.808	5.10	867	3
4	20	323	331	372	384	24	0.689	16.5	31 0	45 5	106 0	75 0	5 42	99 58	152.58	52.49	1.897	2 907	870.00	5.515	2.258	2.09	3.981	1.763	3 20	844	4
5	30	319	321	352	362	20	0.688	13 8	44 8	42 0	148 0	103.2	7.45	97.55	150.55	52.25	1.867	2.881	871.59	5.279	2.268	2.03	3.885	1.713	3.18	822	5
6	40	282	300	316	334	27	0 687	18.5	63 3	35.0	183.0	119.7	8.66	96.34	149.34	50.55	1.906	2 935	872.49	5.504	2.344	1.21	2.393	1.021	1.83	794	6
7	50	267	273	297	306	18	0.686	12.3	75 6	27.0	210.0	134.4	9.72	95.28	148.28	48.81	1.952	3.038	873.29	5.930	2.428	1.06	2.171	0.894	1 51	766	7
8	60	254	261	288	293	9	0.686	6.17	81 77	24 7	234.7	152.9	11.06	53.94	146.54	48.02	1.956	3.052	873.89	5.970	2.468	1.34	2.790	1.130	1.89	753	8
9	70	242	248	268	278	10	0 685	6.85	88.62	21 6	256 3	167.7	12.13	92.87	145.87	47.08	1.973	3.098	875.10	6.112	2.517	1.07	2.272	0 903	1.48	738	9
10	80	234	238	257	263	11	0.684	7.52	96.14	10.5	275.8	179.7	12.99	92.01	145.01	46.20	1.992	3.139	875.54	6.253	2.565	0.86	1.861	0.726	1.16	723	10
11	90	231	233	236	247	21	0 683	14.3	110 44	18.0	293.8	183.4	13.26	91.74	144.74	45.20	2.024	3.202	875.95	6.480	2.622	0.37	0.818	0.312	0.481	707	11
12	100	230	230	231	234	5	0 683	3.42	113.86	17.9	311.7	197 8	14.30	90.70	143.70	44.39	2.043	3.237	876.73	6.613	2.670	0.64	1.441	0 540	0.817	694	12
13	110	247	239	272	252	41	0 684	-28.0	85 86	20 0	331.7	245.8	17.05	87.27	140 27	52.04	1.677	2.695	879.20	4.520	2.277	2.75	5.284	2.321	5.135	712	13
14	120	206	227	217	250	57	0.684	39.0	124.86	17.0	348.7	223.8	15 45	89.55	142.55	51.94	1.724	2.745	877.76	4.732	2.281	1.60	-3.080	-1.350	-2.853	710	14
15	130	195	201	207	212	10	0.683	6.83	131 69	12 0	360 7	229 0	15.84	89.16	142.10	43.06	2.071	3.300	877.79	6.834	2.752	0.16	0.371	0.135	0.198	672	15
16	140	184	190	195	201	12	0.682	8.20	139 9	10 5	361 2	231 3	15 98	89.02	142 07	42.36	2.102	3.359	877.80	7.061	2.797	0.14	0.330	0.118	0.167	661	16

AIR PRESSURE 25 psig

REACTOR FEED: Air - 0.0603 lb moles/hr
NO_2 - 0.0105
NH_3 - 0.0158
Total - 0.0866 lb moles/hr

TABLE VII

ΣK 10,463 ΣT_{GA}^2 7.872.317

ΣT_{GA} 23.303 ΣK_{TGA} 18.486.918

SUMMARY CALCULATIONS REACTION VELOCITY CONSTANT RUN NO. 6

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	1
POINT	LENGTH INCHES	T_p °F	T_{pa} °F	T_g °F	T_{ga} °F	ΔT °F	mC_p $\frac{Btu}{°F\ HR}$	Q_r $\frac{Btu}{HR\ 10^4}$	Q_{ra} $\frac{Btu}{HR\ 10^4}$	Q_b $\frac{Btu}{HR\ 10^4}$	Q_{ba} $\frac{Btu}{HR\ 10^4}$	Q $\frac{Btu}{HR\ 10^4}$	$\frac{\bar{N}_c}{NO_2}$ X 10^4 $\frac{MOLES}{HR}$	$\frac{\bar{N}_r}{NO_2}$ X 10^4 $\frac{MOLES}{HR}$	$\frac{N_r}{NH_3}$ X 10^4 $\frac{MOLES}{HR}$	V $\frac{FT^3}{HR}$	C NO_2 X 10^4 $\frac{MOLES}{FT^3}$	C NH_3 X 10^4 $\frac{MOLES}{FT^3}$	N_t X 10^4 $\frac{MOLES}{HR}$	C NO_2 X C NH_3 X 10^8 $\frac{MOLES^2}{FT^6}$	$\Delta\theta$ X 10^2 SEC	$\frac{\Delta N\ NO_2}{}$ X 10^4 $\frac{MOLES}{HR}$	$\Delta C\ NO_2$ X 10^6 $\frac{MOLES}{FT^3}$	$\frac{\Delta C\ NO_2}{\Delta\theta}$ X 10^4 $\frac{MOLES}{FT^3\ SEC}$	K X 10^{-3} $\frac{FT^3}{MOLES\ SEC}$	T_{ga} °R	POINT
1	0	417	417																								1
2	00	417		417										105.00	158.00	50.00	2.100	3.160	781.00								2
3.	10	334	360	388	403	29	0.637	18.5	19.5	59.0	59.0	40.5	2.93	102.07	155.07	49.27	2.084	3.147	783.20	6.558	2.405	2.93	5.946	2.472	3.77	863	3
4.	20	324	329	372	380	16	0.627	10.0	28.5	45.0	104.0	75.5	5.46	99.54	154.54	48.08	2.070	3.173	785.10	6.568	2.465	2.53	5.262	2.135	3.25	840	4
5	30	297	310	338	355	34	0.626	21.3	49.8	38.5	142.5	92.7	6.72	98.32	151.32	46.74	2.104	3.237	786.04	6.811	2.535	1.22	2.610	1.030	1.51	815	5
6.	40	282	289	317	328	19	0.622	11.8	61.6	32.0	174.5	112.9	8.15	96.89	149.89	45.25	2.141	3.312	787.11	7.091	2.619	1.14	3.160	1.207	1.70	788	6
7	50	270	276	300	309	17	0.619	10.5	72.1	28.0	202.5	130.4	9.44	95.60	148.60	44.21	2.162	3.361	788.08	7.266	2.680	1.29	2.917	1.088	1.50	769	7
8	60	261	265	288	294	12	0.616	7.4	79.5	25.5	228.0	148.5	10.74	94.30	147.30	43.47	2.169	3.389	789.06	7.351	2.726	1.30	2.990	1.097	1.49	754	8
9	70	252	256	278	283	10	0.613	6.1	85.6	23.5	251.5	165.9	12.00	93.04	146.04	42.82	2.173	3.411	790.00	7.412	2.767	1.26	2.942	1.063	1.43	743	9
10	80	244	248	268	273	10	0.611	6.1	91.7	21.5	273.0	161.3	13.11	91.93	144.93	42.29	2.174	3.427	790.83	7.450	2.802	1.11	2.624	0.936	1.26	733	10
11	90	237	240	260	267	8	0.609	4.9	96.6	20.0	293.0	196.4	14.63	90.41	143.41	41.83	2.161	3.428	791.97	7.401	2.832	1.52	3.633	1.283	1.73	724	11
12	100	233	235	256	258	4	0.606	2.4	99.0	19.0	312.0	213.0	15.39	89.65	142.65	41.53	2.159	3.435	792.54	7.416	2.853	0.76	1.830	0.641	0.865	718	12
13	110	226	229	246	251	10	0.615	6.2	105.2	18.0	330.0	225.0	16.26	88.78	141.78	41.15	2.157	3.445	793.20	7.431	2.880	0.87	2.114	0.734	0.988	711	13
14	120	223	224	242	244	4	0.613	2.4	107.6	16.5	346.5	248.9	17.39	87.65	140.65	40.79	2.149	3.448	794.04	7.410	2.905	1.13	2.770	0.954	1.29	704	14
15	130	221	222	239	241	3	0.611	1.8	109.4	16.2	362.7	253.3	18.96	86.08	139.08	40 66	2.117	3.421	795.22	7.242	2.914	1.57	3.862	1.325	1.83	701	15
16	140	217	219	234	237	5	0.610	3.2	112.6	16.0	378.7	264.1	19.09	85.95	138.95	40.46	2.124	3.434	795.32	7.294	2.929	0.13	0.321	0.110	0.15	697	16

AIR PRESSURE 20 psig REACTOR FEED: Air - 0.0518 lb moles/hr
NO_2 - 0.0105
NH_3 - 0.0158
Total - 0.0781 lb moles/hr

TABLE VIII

ΣK 10,560 ΣT_{GA}^2 8,002.800
ΣT_{GA} 22,764 ΣK_{TGA} 17. 689.085

SUMMARY CALCULATIONS REACTION VELOCITY CONSTANT RUN NO. 7

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	1
POINT	LENGTH	T_p	T_{pa}	T_g	T_{ga}	ΔT	mC_p	Q_r	Q_{ra}	Q_b	Q_{ba}	Q	$N_c NO_2 \times 10^4$	$N_r NO_2 \times 10^4$	$N_r NH_3 \times 10^4$	V	$C NO_2 \times 10^4$	$C NH_3 \times 10^4$	$N_t \times 10^4$	$C NO_2 \times C NH_3 \times 10^8$	$\Delta\theta \times 10^2$	$\Delta N NO_2 \times 10^4$	$\Delta C NO_2 \times 10^6$	$\frac{\Delta C NO_2}{\Delta\theta} \times 10^4$	$K \times 10^{-3}$	T_{ga}	POINT
	INCHES	°F	°F	°F	°F	°F	$\frac{Btu}{°F\ HR}$	$\frac{Btu}{HR\ 10^4}$	$\frac{Btu}{HR\ 10^4}$	$\frac{Btu}{HR\ 10^4}$	$\frac{Btu}{HR\ 10^4}$	$\frac{Btu}{HR\ 10^4}$	$\frac{MOLES}{HR}$	$\frac{MOLES}{HR}$	$\frac{MOLES}{HR}$	$\frac{FT^3}{HR}$	$\frac{MOLES}{FT^3}$	$\frac{MOLES}{FT^3}$	$\frac{MOLES}{HR}$	$\frac{MOLES^2}{FT^6}$	SEC	$\frac{MOLES}{HR}$	$\frac{MOLES}{FT^3}$	$\frac{MOLES}{FT^3/SEC}$	$\frac{FT^3}{MOLES/SEC}$	°R	
1	00	383	400																								1
2	00	417												105.00	158.00	43.8	2.397	3.607	698.00								2
3	10	332	348	383	392	17	0.571	9.71	9.71	53.0	53.0	43.3	3.13	101.87	154.87	42.6	2.336	3.552	700.35	8.30	2.712	3.13	7.11	2.62	5.15	852	3
4	20	312	320	355	369	28	0.566	15.9	25.61	42.0	95.0	69.4	5.02	99.93	152.98	42.5	2.352	3.600	701.77	8.47	2.788	1.89	4 45	1 60	1.89	829	4
5	30	305	307	345	350	10	0.566	5.66	30.27	37.0	132.0	101.7	7.35	97.65	150.65	41.6	2.347	3.621	703.51	8.50	2.848	2.33	5.60	1.97	2.32	810	5
6	40	292	299	335	340	10	0.569	5.67	35.94	35 0	167 0	131.1	9.48	95.52	148.52	41.2	2.318	3.605	705.11	8.36	2.876	2.13	5.17	1.80	2.15	800	6
7	50	283	288	317	326	18	0 562	10 15	46 09	31.2	198.2	152.1	11.00	94.00	147.00	40.5	2.321	3 630	706.25	8.42	2.925	1.52	3.75	1.28	1.53	786	7
8	60	274	279	306	312	11	0.561	6 17	52 26	28 2	226.4	174.1	12.59	92 41	145 41	39.9	2.316	3.644	707 44	8.44	2.969	1.59	3.98	1.34	1 59	772	8
9	70	267	272	298	302	8	0 560	4 48	56 74	27.0	253 4	196.7	14 22	90 78	143 78	39 4	2.304	3 649	708.67	8.41	3 007	1 63	4 14	1 38	1.64	762	9
10	80	259	263	287	293	11	0 559	6 15	62 89	25.0	278.4	215 5	15 58	89 42	142.42	39.0	2.270	3.652	709 69	8 29	3.038	1.36	3.49	1.15	1 39	753	10
11	90	254	257	280	284	7	0.558	3 91	66 80	23 5	301 9	235 1	17 00	88.00	141 00	38.6	2 280	3 653	710.75	8 33	3 069	1 42	3 68	1.20	1.44	744	11
12	100	252	253	278	279	2	0 557	1 11	67 90	22 5	323 4	255 5	18 47	86 53	139 53	38.4	2.253	3.634	711.85	8.19	3.085	1.47	3.83	1.24	1.51	739	12
13	110	244	248	267	273	11	0 556	6.12	74.02	21 0	344 4	270 4	19 55	85 45	138.45	38.1	2.243	3.634	712.66	8.15	3.110	1.08	2 83	0 910	1 12	733	13
14	120	243	243	266	266	1	0.555	0.56	74.58	20.5	364 9	290 3	20 99	84 01	137.01	37.8	2.205	3.625	713 74	7 99	3 134	1.45	3.84	1 22	1.53	726	14
15	130	241	242	263	265	3	0 554	1 11	75 69	20 3	385 2	309 5	22.38	82 62	135.62	38.8	2.186	3.588	714.79	7.84	3.135	1.39	3 68	1.17	1 49	725	15
16	140	236	239	260	262	3	0.553	1 11	76 80	20 0	405.2	328.4	23.75	81.25	134.25	37.7	2.155	3 560	715.81	7.67	3.143	1 37	3.73	1.155	1.51	722	16

AIR PRESSURE 15 psig REACTOR FEED: Air- 0.0435 lb moles/hr
NO_2- 0.0105
NH_3- 0.0158
Total- 0.0698 lb moles/hr

TABLE IX

ΣK 10,749 ΣT_{GA}^2 8. 265.129

ΣT_{GA} 24.260 ΣK_{TGA} 18.846.780

SUMMARY CALCULATIONS REACTION VELOCITY CONSTANT RUN NO. 8

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	1
POINT	LENGTH INCHES	T_p °F	T_{pa} °F	T_g °F	T_{ga} °F	ΔT °F	mC_p $\frac{Btu}{°F\ HR}$	Q_r $\frac{Btu}{HR\ 10^n}$	Q_{ra} $\frac{Btu}{HR\ 10^n}$	Q_b $\frac{Btu}{HR\ 10^n}$	Q_{ba} $\frac{Btu}{HR\ 10^n}$	Q $\frac{Btu}{HR\ 10^n}$	$\frac{N_c\ NO_2}{X\ 10^4}$ $\frac{MOLES}{HR}$	$\frac{N_r\ NO_2}{X\ 10^4}$ $\frac{MOLES}{HR}$	$\frac{N_r\ NH_3}{X\ 10^4}$ $\frac{MOLES}{HR}$	V $\frac{FT^3}{HR}$	$\frac{C\ NO_2}{X\ 10^4}$ $\frac{MOLES}{FT^3}$	$\frac{C\ NH_3}{X\ 10^4}$ $\frac{MOLES}{FT^3}$	$\frac{N_t}{X\ 10^4}$ $\frac{MOLES}{HR}$	$\frac{C\ NO_2 \times C\ NH_3}{X\ 10^8}$ $\frac{MOLES^2}{FT^6}$	$\Delta\theta$ X 10^2 SEC	$\frac{\Delta N\ NO_2}{X\ 10^4}$ $\frac{MOLES}{HR}$	$\frac{\Delta C\ NO_2}{X\ 10^6}$ $\frac{MOLES}{FT^3}$	$\frac{\Delta C\ NO_2}{\Delta\theta}$ X 10^4 $\frac{MOLES}{FT^3\ SEC}$	K X 10^3 $\frac{FT^3}{MOLES\ SEC}$	T_{ga} °R	POINT
1	00	451	477																								1
2	00	493		477										105.00	151.00	53.4	1.966	2.959	781.00								2
3	10	368	400	436	437	41	0 637	26.1	26.1	78.5	78.5	52.4	3.79	101.21	154.21	51.3	1.973	3.006	783.83	5.931	2.310	3.79	7.388	3.198	5.39	917	3
4	20	344	353	403	420	33	0.635	21.0	27.1	54.2	132.7	85.6	6.19	98,81	151.81	49.5	1.996	3.067	785.64	6.122	2.394	2.40	4.848	2.025	3.31	880	4
5	30	324	335	372	388	31	0.625	19.4	66.5	47.5	180.2	113.7	8.22	96.78	149.78	47.8	2.025	3.133	787.17	6.304	2.479	2.03	4.247	1.774	2.81	848	5
6.	40	311	315	352	362	20	o.625	12.5	79.0	40.0	220.2	141.2	10.21	94.79	147.79	46.7	2.030	3.165	788.66	6.425	2.537	1.99	4.261	1.719	2.73	822	6
7.	50	305	308	345	349	7	0.625	4.38	83.38	37.7	257.9	184.5	13.34	91.66	144.64	46.3	1.980	3.124	790.99	6.186	2.559	3.13	6.760	2.642	4.11	809	7
8	60	296	301	334	340	11	0.625	6 88	90.26	35.0	292.9	202.6	14.65	90.35	143.35	45.9	1.968	3.123	791.98	6.146	2.589	1.31	2.854	1.105	1.80	800	8
9	70	287	292	322	328	12	0.625	7.50	97.76	32.0	324.9	227.1	16.42	88.58	141.58	45.3	1.955	3.125	793.32	6.109	2.616	1.77	3.907	1.494	2.45	788	9
10	80	277	282	310	316	12	0.625	7.50	105.26	30.0	354.9	249.6	18.05	86.95	139.95	44.7	1.945	3.131	794.54	6.089	2.651	1.64	3.669	1.384	2.27	778	10
11	90	271	274	302	306	8	0.625	5.00	110.26	27.5	382.4	272.1	19.67	85.33	138.33	44.3	1.926	3.123	795.75	6.015	2.675	1.62	3.657	1.367	2.27	766	11
12	100	268	270	298	300	4	0.625	2.50	112.76	27.0	409.4	296.7	21.45	83.55	136.55	44.1	1.895	3.096	797.08	5.867	2.687	1.78	4.036	1.502	2.56	760	12
13	110	263	266	293	296	5	0.625	3.12	115.88	26.7	436.1	320.2	23.15	81.85	134.85	43.9	1.864	3.072	798.36	5.726	2.699	1.80	4.100	1.519	2.65	756	13
14	120	265	254	295	294	-2	0.625	-1.25	114.63	26.6	462.7	348.1	25.17	79.83	132.83	44.1	1.810	3.012	799.88	5.542	2.687	2.02	4.580	1.704	3.12	754	14
15	130	265	265	295	295	0	0.625	0.00	114.63	26.6	489.3	374.7	27.09	77.91	130.91	44.2	1.763	2.962	801.32	5.222	2.680	1.92	4.344	1.621	3.10	755	15
16	140	261	263	288	292	7	0.625	4.38	119.00	26.5	519.8	397.8	28.63	76.37	129.37	43.8	1.744	2.954	802.47	5.152	2.705	1.54	3.516	1.230	2.39	752	16

AIR PRESSURE 20 psig REACTOR FEED: Air - 0.0518 lb moles/hr
NO_2 - 0.0105
NH_3 - 0.0158
Total - 0.0781 lb moles/hr

TABLE X

ΣK 11,183 ΣT_{GA}^2 8,967.615

ΣT_{GA} 40,970 $\Sigma K T_{GA}$ 33.125.100

Column 5. Tg - Temperature of the gas corresponding to Tp taken from Figure 5 page 33.

6. Tga - Mean temperature of gas in section, an average of Tg at beginning and end of section

7. ΔT - Loss of temperature by the gas in the section difference in Tg entering and leaving section

8. mCp - $mCp_{tga} = NrNO_2Cp_{T_{ga}}NO_2 + NrNH_3Cp_{T_{ga}}NH_3 + NrAirCp_{T_{ga}}Air + Nr_{H_2O}\ Cp_{T_{ga}}H_2O$

Heat capacities of the components of the reactant stream at various temperatures are given in Table XI

9. Qr - Apparent heat loss of section Column 7 X Column 8.

$$Qr = mCp\Delta T$$

10. Qra - Accumulated apparent heat loss, Qr accumulated

11. Qb - Apparent heat loss from section as determined from blank runs, values taken from Figure 6 page 38 at Tpa of section

12. Qba - Accumulated apparent heat loss Qb accumulated

13. Q - Heat of reaction Qba - Qra

14. $NcNO_2$ - Pound moles of NO_2 consumed in reaction

$$NcNO_2 = Q/138,300$$

15. $NrNO_2$ - Pound moles of unreacted NO_2 in the reactant stream from relation (1) page 36

$$NrNO_2 = NiNO_2 - NcNO_2$$

Column 16. $NrNH_3$ - Pound moles of unreacted NH_3 in the reactant stream from relation (2) page 36

$$NrNO_2 = NiNH_3 - NcNO_2$$

17. V - Volume of the reactant stream at Tga and 1 atmosphere pressure

$$V = nRT/P$$

$$V = Nt(0.73)(Tga + 460)$$

18. CNO_2 - Concentr tion of NO_2 in the section, Column 15/Column 17

$$CNO_2 = NrNO_2/V$$

19. CNH_3 - Concentration of NH_3 in the reactant stream, Column 16/Column 17

$$CNH_3 = NrNH_3/V$$

20. Nt - Total moles in reactant stream from relation (5) page 36

$$Nt = Nt_i + 0.75\ NcNO_2$$

21. CNO_2CNH_3 - Column 18 X Column 19

22. $\Delta\Theta$ - Time required for reactants to pass thru section, 1.185/Column 17

$$\Delta\Theta = 1/VSL$$

where, V = volume of reactants in cubic feet per hour

S = cross sectional area of reactor in square feet, $3.95X10^{-4}ft^2$

L = length of reactor section in feet, 10/12 ft

$$\Delta\Theta = 1.185/V$$

Column 23. ΔNNO_2 - The change in $NrNO_2$ in the section, difference in $NrNO_2$ at beginning and end of section

24. ΔCNO_2 - The change in concentration of NO_2 in the section, Column 23/Column 17

$$\Delta CNO_2 = \Delta NNO_2/V$$

25. Column 24/Column 22

26. Column 25/Column 21

27. Tga mean temperature of gas in °R, Column 6 + 460°F

The values of the reaction velocity constants calculated and tabulated in Tables VII, VIII, IX and X are plotted as a function of mean gas temperature in Figure 7 page 45.

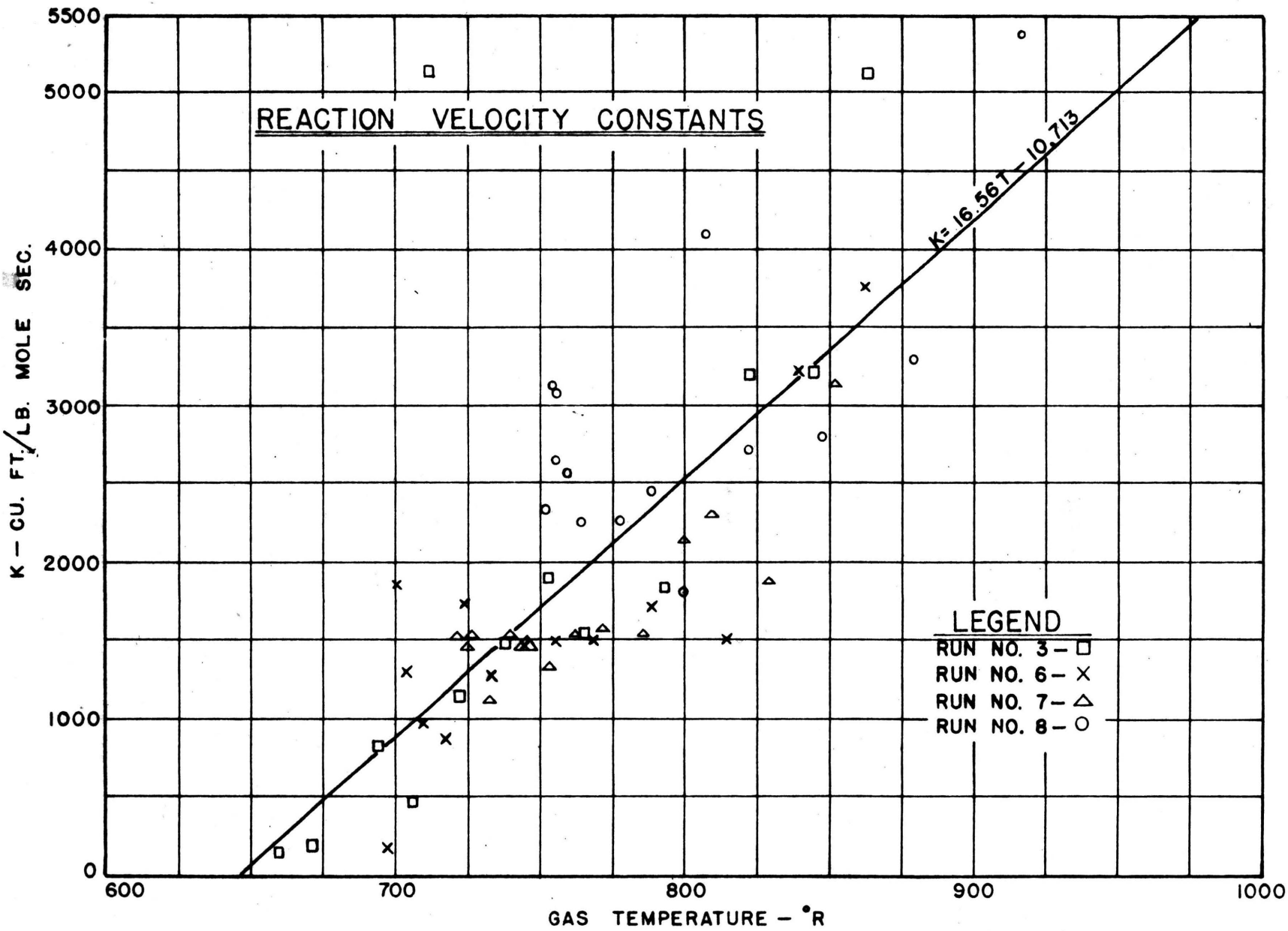
REACTION VELOCITY CONSTANTS
K= 16.56 T - 10,713
LEGEND
RUN NO. 3 - □
RUN NO. 6 - ×
RUN NO. 7 - △
RUN NO. 8 - ○
K - CU. FT./LB. MOLE SEC.
GAS TEMPERATURE - °R
0
1000
2000
3000
4000
5000
5500
600
700
800
900
1000

Figure 7

Developement of the equation for the reaction velocity constant as a function of absolute gas temperature:

Due to the wide scattering of points the developement of a polynomial equation was not justified, so the equation was developed in the linear form, K=(a)Tga + b, by the method of least squares.

The summations of the variables were taken from Tables VII, VIII, IX, and X and are as follows:

$$K = 111,300$$

$$Tga = 42,949$$

$$Tga^2 = 33,107,861$$

$$KTga = 88,147,880$$

$$n = 56$$

$$(1) \quad an + (b)Tga - K = 0$$

$$(2) \quad (a)Tga + (b)Tga^2 - KTga = 0$$

$$(1) \quad 56a + 42,949b - 111,300 = 0$$

$$(2) \quad 42,949a + 33,107,861b - 88,147,880 = 0$$

Solving equations (1) and (2) simultaneously:

$$a = -10,713$$

$$b = 16.56$$

therefore the final equation is:

$$K = 16.56Tga - 10,713 \quad T-°R$$

TABLE XI

CRITICAL FLOW ORIFICES

CALIBRATION

AIR PRESSURE UPSTREAM psig	OBSERVED FLOW ORIFICE NO. 1 lb air/hr	OBSERVED FLOW ORIFICE NO. 2 lb air/hr	COMBINED FLOW lb air/hr
15	0.632	0.630	1.262
20	0.751	0.750	1.501
30	1.014	1.010	2.024
40	1.280	1.276	2.556
50	1.501	1.495	2.996
60	1.726	1.719	3.445

MEAN CONSTANT C_v = 0.870

DIAMETER OF ORIFICES = 0.023"

Lb Moles/ Hr = Lb/Hr (1/29)

TABLE XII

FLOWRATOR

CALIBRATION

FLOWRATOR READING	OBSERVED FLOW NITROGEN DIOXIDE g moles/min X 10^3	AMMONIA g moles/min X 10^3
3	19 8	28.3
4	24.1	36.6
5	30.0	44 6
6	35.7	54.6
7	42.5	64.4
8	47.7	74.5
9	55.5	84.7
10	62.0	94.5
11	68.3	104.8
12	75.7	115.0
13	83.0	125.0
14	90.2	135.1

g moles NO_2/min (6.08) = lb NO_2/hr

g moles NH_3/min (2.25) = lb NH_3/hr

lb No_2/hr (1/46) = lb moles NO_2/hr

lb NH_3/hr (1/17) = lb moles NH_3/hr

Fisher-Porter Flowrators using tube no. 06-150/13 with stainless steel float 3/16"

TABLE XIII

MOLAL HEAT CAPACITIES

100-500 °F

Btu/lb mole °F

TEMPERATURE	NO_2	NH_3	AIR	H_2O
100	8.95	8.55	6.58	
200	9.45	8.95	6.97	7.98
300	9.85	9.39	7.40	8.06
400	10.30	9.78	7.95	8.12
500	10.65	10.19	8.68	8.19

$C_p\ NO_2 = 5.48 + 7.58 \times 10^{-3}T - 2.60 \times 10^{-6}\ T^2$ T-°R (19)

$C_p\ NH_3 = 3.29 + 4.98 \times 10^{-3}T - 9.78 \times 10^{-7}\ T^2$ T-°R (19)

C_p AIR (19)

$C_p\ H_2O$ (20)

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DISCUSSION AND SUMMARY OF RESULTS

The initial attempt to get quantitative kinetic data on the reaction between ammonia and nitrogen dioxide at initial temperatures of 80° - 90°F met with failure due to the large amounts of solid products formed and the subsequent clogging of the reactor. However, some qualitative conclusions can be drawn as to the nature of the reaction and its temperature limits. Apparently, at initial temperatures of 80° - 90° the reaction is relatively slow but the rate increases rapidly with increase in temperature to some undetermined point in the vicinity of 180°F where the formation of solid products ceases completely. These facts were deduced first from observation of the reaction in a glass reactor tube. Upon introduction of the reactants into the reactors the reaction, as evidenced by the formation of a white smoke, would start at some point 3 - 5 feet from the point of mixing then rapidly advance toward the mixing chamber as the heat of reaction warmed the reactor, until the reaction was taking place at the point of mixing. Soon thereafter the reactor would become clogged with solid products. Second, that in later runs with initial temperatures well above 180°F there was no evidence of solid products in the exaust gases from the reactor unless the temperature in the final stages of the reactor fell to below 180°F in which case solid products were observed in the reactor exaust.

It was first considered that the normal disproportionation reaction of NO_2 to form HNO_2 and HNO_3 with water vapor present in the air then further reaction with NH_3 to form NH_4NO_2 and NH_4NO_3 was responsible for the formation of solid products. However, a qualitative analysis of the solid products showed the absence of the nitrite radical. More detailed and quantitative data than that obtained during this study would be required to determine the mechanism of the reaction at temperatures below 180°F.

In the course of the experimental work a qualitative run was made in which the reactants were impinged against a metal surface heated to approximately 1000°F in a single heater of the type shown in Figure 4, page 17. In this run the reaction was completed in the reactor as evidenced by the complete lack of color of the exaust gases. From temperature indication noted it appeared that the reaction was complete within the 10" section of reactor immediately following the heater. So it is apparent that the reaction is exceeding fast at elevated temperatures.

The data presented in the previous section is for the reaction at temperatures ranging from 200 - 450°F, in this range there is no evidence of the formation of solid products and the reaction appears to be relatively slow. The reaction velocity constant was shown to increase with temperature as would be expected. In Run No. 8 with an initial temperature of 477°F and intermediate concentration of

reactants the reaction was about 28% complete in 0.35 sec. In Run No. 6 with the same concentration of reactants and an initial temperature of 417°F the reaction was 19% complete in 0.37 sec. In Run No. 3 with initial temperature of 417°F and lowest concentrations the reaction was about 16% complete in 0.35 sec and in Run No. 7 initial temperature of 400° and the highest concentration the reaction was 24% complete in 0.41 sec. So it is apparent qualitatively that the rate of reaction is increased by increased temperature and concentration of reaction. More extensive data would be required to establish the relationship between concentration, temperature and the reaction velocity constant.

The reaction velocity constants evaluated in this work are subject to the inherent inaccuracies of calculated heat transfer coefficient and gas temperatures derived from pipe wall temperatures and the assumptions made are not fully established. However, the trend of the results indicate that the apparatus as used in this study, with further refinements designed to eliminate sources of error due to calculated heat transfer values would be a practical instrument for evaluating reaction velocity constants of gas phase reactions of the ammonia-nitrogen dioxide type.

CONCLUSIONS

The reaction between ammonia and nitrogen dioxide in the temperature range above 200°F produces only gaseous products and the reaction velocity constant for the range 660° - 910°R is related to temperature by the equation:

$$K = 16.56T - 10,713 \quad T - °R$$

The continuous flow reactor designed for this study was proven practical for the kinetic study of gas phase reactions in which no solid products are formed. Due to the inherent inaccuracies of calculations derived from indirect heat transfer data, it is believed that the following modification of the reactor would largely eliminate this source of error and produce an instrument for more accurate evaluations of the reaction velocity constants of this type of reaction.

The reactor be modified so that the ambient temperature of each section could be controlled to the temperature of the gas at the mid-point of each section, this in effect would produce a truly adiabatic reactor and the losses of heat from the reactor negligible. It is also believed that with such a reactor, the point at which the solid product reaction ceases could be determined.

This modification could be made by inserting thermocouple wells in the reactor at intervals of 10" - 12" so they would sense the actual temperature of the gas stream. Enclose the 1/8" pipe reactor tube in a larger pipe leav-

ing a dead air space surrounding the reactor tube. Set thermocouple junctions in the surface of the larger pipe at points opposite those in the reactor. Provide each section with a heating coil extending between the mid-point between adjacent thermocouple and provide suitable means of voltage control to the heating coil. Automatic control of the surface temperature of the outer wall to that of the gas stream would be desirable but not necessary as point to point manual control would be possible by use of an electronic null point indicator and a variable transformer.

It is believed that the reactor so modified would permit the reaction to be studied over a much wider range of initial temperatures and permit wider variations in initial reactant concentrations. With this wider range of experimental conditions sufficient data could be obtained to extend the range of K to T relations and more accurately establish the correlation between the two. Further, the order of reaction could be established.

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VITA

Ormond Kennedy Lay was born in South Bend, Indiana, May 2, 1911 and later made his home in St Louis, Missouri, where he attended elementary school. He was graduated from Cleveland High School in St Louis, Missouri, in June 1928. He enrolled in the Missouri School of Mines and Metallurgy in September 1928 from which he received a Bachelor of Science Degree in Chemical Engineering in May 1932.

He was married on December 17, 1931 to Lillian Marion Roach of Rolla, Missouri, and has two children. Barbara Ruth Lay born in Pittsburgh, Pennsylvania, March 10, 1939 and Janet Kay Lay, born at Camp Forrest, Tennessee, July 25, 1942.

After his graduation in 1932, he pursued a career in the laundry industry, both as a technical sales engineer and in managerial capacities until the advent of World War II. He served with the United States Army for five years as Technical Laundry Advisor to the Quartermaster General. He was returned to inactive duty in April 1945 as a Lieutenant Colonel, Quartermaster Corps.

Following his tour of duty in the Army, Mr. Lay entered the laundry and dry cleaning business in Dallas, Texas, which business he conducted until his health failed in 1948. After two years hospitalization recuperating from his illness he reentered the Missouri School of Mines and

Metallurgy in September 1950, to review undergraduate work and to obtain a Masters degree in Chemical Engineering. He served as a Graduate Assistant in Chemical Engineering for the 1951-2 school year and as an Instructor in Chemical Engineering since September 1952.